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14. ABSTRACT This grant permitted construction of instrumentation for monitoring excited state photoisomerization using femtosecond stimulated Raman spectroscopy, a particularly informative means of following molecules as they evolve in the excited state. The heart of the instrument is a modern, regeneratively amplified ultrafast Ti:sapphire laser. That laser and associated devices enable experiments using a combination of sophisticated excitation schemes and sophisticated detection methods. These photoisomerization experiments probe the role of excited state vibrations in determining the competition among isomerization pathways and are potentially a means of controlling rearrangements. The experiments provide new insights into fundamental processes, test theoretical descriptions, and uncover the detailed behavior of molecular devices.					
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**Final Technical Report
FA9550-08-1-0277 (DURIP)**

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Introduction

Molecular photoswitches and molecular machines are common in nature, as illustrated by the photoisomerization of *cis*-retinal that lies at the heart of vision and the geometry change of myosin during molecular transport and muscle function. The possibility of tailoring molecules to function as circuit elements or storage devices or molecular machines animates a rich and growing field in which there are both practical and fundamental questions to answer. For example, the use of a photoswitch as a transducer for coupling light into a molecular circuit or the use of a photochromic molecule as an optical storage medium requires the correct interaction with light, suitable excited state dynamics, and favorable interactions with the surroundings. Similarly, the construction of nanomachines requires molecules that function as molecular rotors, hinges, or other mechanical devices driven by external stimuli. In cases where the external stimulus is a photon, it is obvious that understanding the photoinduced dynamics is essential, but even for other stimuli, such as electron injection, the subsequent dynamics are likely to be closely related.

The goal of our studies is understanding the interaction of coupled electronic states and their influence on the nuclear dynamics in molecules that contain the central elements of molecular electronic devices and molecular machines. Because vibrations provide clear spectroscopic signatures of the motion of the nuclei, an essential part of our approach is probing vibrations of the molecule as it changes geometry. Our goal is to explore the influence of the environment incisively and to discover the consequences of initial vibrational excitation for the excited state dynamics. Understanding the role of vibrations and electronic excitation on the pathways and dynamics in excited molecules potentially leads to control of excited state processes by initial vibrational state preparation. These studies grow out of approaches that we have already established with AFOSR support and are now extending to study new dynamics in practically important systems.

Instrumentation

This instrumentation grant has allowed us to assemble a versatile and reliable apparatus for probing vibrational structure with good time and spectral resolution in order to follow excited state isomerizations in prototypical and in practically important molecules. We currently have operating improved versions of our broadband transient absorption experiments using array detection and the first version of our new femtosecond stimulated Raman scattering experiments. The new apparatus incorporates recent developments in the production of well-controlled ultrashort pulses.

A modern Ti:sapphire laser using chirped pulse amplification to produce 3.8-mJ, 35-fs duration pulses of 800-nm light at 1 kHz is the heart of the apparatus. We produce electronic

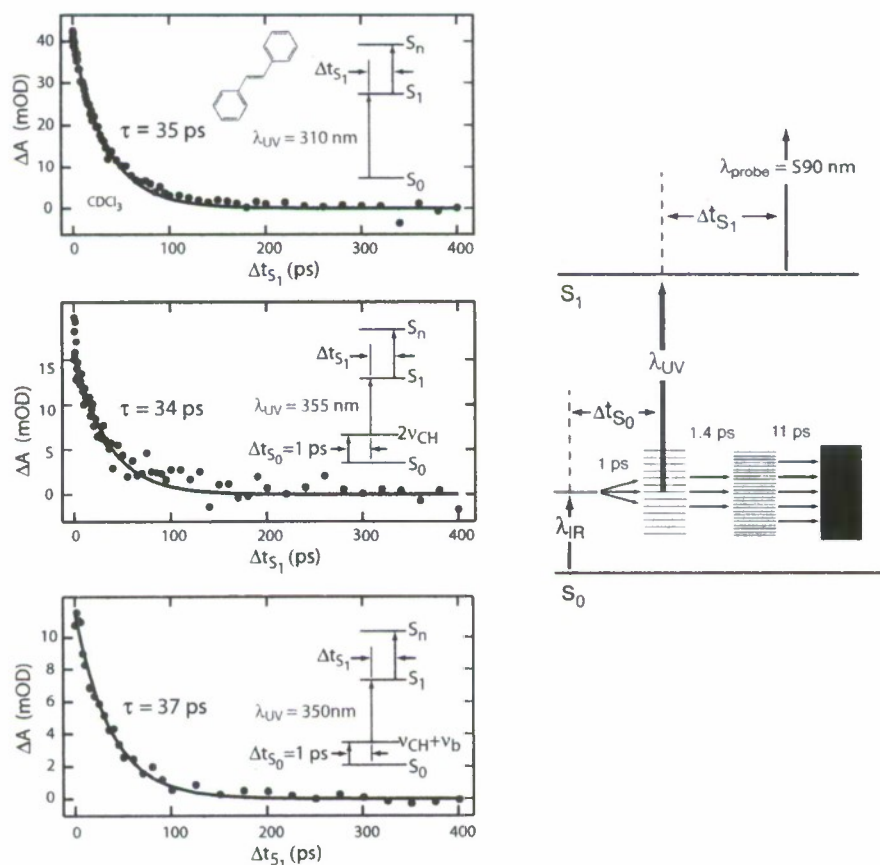
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excitation pulses using non-collinear optical parametric amplification of a portion of the frequency doubled (400 nm) fundamental from the Ti:sapphire laser. Similarly, we generate a continuum probe by focusing a small portion of the fundamental into a CaF₂ or sapphire substrate as. The relatively large energy and short duration of the pulses from the Ti:sapphire laser makes both of these processes efficient.

The short pulses give excellent time resolution, and the laser system improves every aspect of our AFOSR funded work. It now permits experiments that were previously impossible. The more powerful pulses allow us to generate both infrared and ultraviolet light for initial excitation while also generating the tunable, narrowband and continuum pulses for femtosecond stimulated Raman spectroscopy. This modern laser is allowing us to put several different techniques together for informative and wide-ranging studies. We are now able to combine sophisticated excitation and sophisticated detection to follow the evolution of the system. The DURIP grant is also making it possible for us to generate shaped infrared pulses to introduce even more specific vibrational excitation in our target molecules.

Vibrationally Mediated Photoisomerization Measurements

The data shown in the Figure illustrate the measurements we can now make with the simplest incarnation of the improved apparatus. In these experiments, we excite stilbene to its electronically excited state (S_1) where it isomerizes by passage through a conical intersection with the ground state (S_0). We observe its decay on the excited state by monitoring a transition



to a higher electronic state (S_n) with a broadband continuum pulse. The decay in the top trace gives the lifetime after direct excitation to S_1 . The other two show the decay after excitation to the same total energy on S_1 but following initial excitation of a ground state vibration with an infrared pulse. Such measurements allow us to explore excited state dynamics in new detail and to learn about the effect of initial vibrational excitation on the excited state dynamics in liquids.

This new experimental capability has not only extended the scope of the experiments we can perform, but it has also expanded the educational horizons of students and post-doctoral associates. Assembling the apparatus and making the first measurements has been a marvelous opportunity for the people working on our AFOSR funded research, and in the longer term, the laboratory will provide a breadth of opportunity for young scientists who join the project over the next several years. The benefits extend beyond those actually working with the apparatus as it broadens the expertise in our entire group as well as being an aspect of technology development that we can share with other research groups in our Department. Finally, these experiments open the possibilities of collaboration with theorists and researchers concerned with practical molecular devices that would be impossible otherwise.